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# Physikalisches Institut

SINGLE PARTICLE ORBITALS FOR CONFIGURATION INTERACTION
DERIVED FROM QUANTUM ELECTRODYNAMICS

Klaus Dietz

and

Bernd A. Heß

Institut für physikalische und theoretische Chemie
der Universität Bonn
Wegelerstr. 12
D-5300 Bonn 1
W-Germany

Abstract:

By explicitly introducing degrees of freedom for the electromagnetic field into the Hamiltonian for an N-electron system, we propose a variational procedure leading to mean fields different from the Hartree-Fock field. We show that g-Hartree equations obtain if the electromagnetic field is assumed to be in a coherent state. Since the solutions of these equations, the g-Hartree orbitals, are derived from a variational ansatz more general than the Hartree-Fock functional, we expect them to be particularly suitable to furnish a single-particle basis set for fast converging configuration interaction (CI) calculations. We report configuration interaction studies on the water molecule in a double zeta basis set employing various single-particle basis set transformations for the construction of the configuration state functions and investigate the convergence behaviour of the CI expansion explicitly.

We find that the expansion in terms of g-Hartree orbitals receives substantially larger fractions of the total correlation energy in the case considered, if single excitations with respect to the mean field configuration are retained in the CI procedure.

# 1. INTRODUCTION

The convergence of the configuration interaction (CI) expansion of multiparticle wave functions in atomic and molecular structure calculations depends strongly on the single-particle orbitals used for the construction of the configuration state functions (CSF's) spanning the multiparticle basis of the CI space [1]. Moreover, the single-particle picture enters at the very beginning of a molecular structure calculation, because in this case the aforementioned orbitals are commonly expanded in a fixed basis set of suitable functions using the "linear combination of atomic orbitals" (LCAO) approach. In this approximation the results of a mean field calculation and an ensuing CI treatment, of course, depend on the basis set. The common procedure to determine the parameters of the basis functions comprises a direct minimization of the total energy of the constituent atoms in the Hartree-Fock approximation. In most cases, the variation is carried out for a fixed number of basis functions in a given irreducible representation of the atomic symmetry group. Of course, only the parameters of functions spanning occupied orbitals may be determined in this way, whereas the calculation of the correlation energy (which is the difference of the Hartree-Fock energy and the lowest eigenvalue of the exact non-relativistic Hamiltonian) requires also the determination of virtual orbitals, notably of higher angular momentum. For calculations of this type, the basis set is commonly augmented by additional functions designed to "correlate" the occupied single-particle functions. In practice, functions of higher angular momentum having spatial extension similar to the occupied orbital in question are employed for this purpose. The distortion of the charge distribution in the course of molecule formation may require further flexibility, which is accounted for by inclusion of "polarization functions" [1].

Thus the single-particle picture enters at two stages of the calculation, and often the Hartree-Fock method is used to provide the single particle basis set also for the construction of configuration state functions for the CI expansion, hereafter called the "molecular orbital" (MO) basis set. It is by no means obvious, however, that the determination of an LCAO basis set or an MO basis set by the Hartree-Fock mean field is an optimal choice regarding the convergence of the CI expansion. On the contrary, full CI investigations for small systems show that the perturbation series around the Hartree-Fock field (in a given LCAO basis set) converges slowly when the correlations are large [2], and it was known long before that the so-called natural orbitals, i.e. the eigenfunctions of the CI density matrix, satisfying certain optimum criteria [3-5], are particularly suitable for the construction of the CI basis set.

These findings have been employed in various methods, starting with approximate natural orbitals, to devise schemes for particularly fast converging CI expansions [6-8].

The optimum criteria fulfilled by natural molecular orbital basis sets do not imply, however, that a CI expansion of prescribed length (say a full singles-doubles (SD) CI, i.e. a CI comprising all configurations that may be obtained by single or double substitutions of the orbitals of a reference configuration) yields in any case a lower expectation value of the total energy as compared to Hartree-Fock MO's. This is the case only for CI expansions of lower quality than a SD-CI, as has been shown by explicit calculations [9]. For a full SD-CI, the correlation energy obtained from natural orbitals may well be slightly smaller than the corresponding value calculated from a Hartree-Fock molecular basis.

The explanation for this finding is the fact that the energy of a "full class" CI calculation (i.e. a full CI in a space containing all configurations of a certain excitation class, e.g. single, double, triple etc.) is invariant with respect to unitary transformations within the set of occupied orbitals and separately invariant with respect to unitary transformations within the set of virtual orbitals [1]. The boundary of occupied and virtual orbitals is, however, approximately retained in the natural orbital transformation, as may be seen from the fact that the "first natural function" (i.e. the Slater determinant made up from strongly occupied natural orbitals) has overlap near to one with the Hartree-Fock determinant in the case that the latter has large weight in the final wave function [5].

As a consequence, the full class wave functions yield very similar energies in the case of Hartree-Fock- and natural molecular orbitals. Since other schemes like "improved virtual orbitals" (IVO) [10-12] or "internally consistent self-consistent field (ICSCF)" orbitals [13-14] implement unitary transformations in the virtual orbital space, we expect in these cases, too, that the expectation values of full class wave functions are very similar to the results obtained from Hartree-Fock orbitals. The determination of an optimised single particle basis for CI calculations obviously requires a subtle mixing between the occupied and unoccupied orbitals. In order to achieve progress in this field, it seems to be necessary to study first the impact of the underlying fundamental theory, namely Quantum Electrodynamics, on this problem. We show that by explicitly introducing degrees of freedom for the electromagnetic field into the variational calculation for the single particle states we arrive at a new type of orbitals previously derived in a different context [15], the g-Hartree orbitals. Starting from this result, we derive and test a computational procedure for the use of g-Hartree orbitals in CI calculations.

## 2. SINGLE-PARTICLE ORBITALS IN NON-RELATIVISTIC AND RELATIVISTIC QUANTUM ELECTRODYNAMICS

In this chapter we shall undertake to introduce a general framework for the construction of single-particle orbitals for localised many-electron systems. We shall use quantum field theory, more precisely quantum electrodynamics (QED), as the general scope for our derivations. This has several, in our view sometimes decisive advantages; we have to explain why. Needless to say, this explanation is a long and complex story. To abbreviate it we first enumerate a few points which we then discuss in some detail.

i) Symmetry properties of many-electron states are automatically ensured. It is a well-known fact that commutation and anti-commutation properties of quantum fields guarantee Bose-Einstein and Fermi-Dirac statistics.

ii) We have universality in the following sense: there is one and only one Hamiltonian for many-electrons systems like atoms, molecules and solids, external degrees of freedom distinguishing the three cases.

iii) QED is the only known theoretical framework allowing for an unambiguous formulation of the relativistic many-electron problem.

There are essentially two ways: one either derives relativistic many-body Schrödinger equations [16] from the QED-Hamiltonian or one extracts [17] a relativistic mean-field picture together with its single-particle basis. Both methods avoid double-counting problems since they start from a clear-cut starting point, a theory, namely QED, which is known to be confirmed by the most precise measurements of all physics; more ad hoc constructions, for instance "three-body forces" easily lead to double counting and, therefore, are doomed to failure [18]. Theoretically, the method of extracting many-body Schrödinger equations will encounter, at a certain stage, the problem that no renormalisation algorithm is known at present; mean-field methods allow for conventional renormalisation.

iv) The field-theoretic approach guarantees the scaling properties ensuing from the electromagnetic interaction of electrons and leads to their explicit formulation in terms of renormalisation group equations [19].

The latter can be used as a tool in the search of optimal finite-dimensional basis sets for the approximation of spectral properties of many-electron systems.

v) As a corollary to (ii), we have a universal equation of motion: the Schrödinger equation of QED.

This equation is at the center of our further considerations. We choose Coulomb gauge and write

$$(i\partial_t - H)\Psi = 0 \tag{2.1}$$

where

$$H = \int d^3x\; \varphi^*(\vec{x}) A \varphi(\vec{x}) + \frac{1}{2}\int\int d^3x\, d^3x'\, \varphi^*(\vec{x}) \varphi^*(\vec{x}') V(\vec{x},\vec{x}') \varphi(\vec{x}') \varphi(\vec{x}) \tag{2.2}$$

$\varphi(\vec{x})$ is the electron field, time-independent in the Schrödinger picture; $V(\vec{x},\vec{x}')$ is the Coulomb potential and describes the electron-electron interaction

$$V(\vec{x},\vec{x}') = \frac{e^2}{4\pi} \frac{1}{|\vec{x}-\vec{x}'|}. \tag{2.3}$$

The differential operator A stands for the single-particle dispersion and reads in the non-relativistic case

$$A = -\frac{1}{2m}\Delta + V_{ext}(\vec{x}) \tag{2.4}$$

where $V_{ext}(\vec{x})$ is the nuclear Coulomb potential or, in the case of molecules, a collection of nuclear Coulomb potentials which, in the Born-Oppenheimer approximation, are not endowed with kinetic degrees of freedom.

This Hamiltonian also describes the electron degrees of freedom in the relativistic case (Coulomb gauge assumed); we simply have to reinterpret $\varphi(\vec{x})$ as a Dirac-spinor field and implement relativistic kinematics by taking the single particle dispersion as (we do not write explicitly transverse electromagnetic degrees of freedom)

$$A = \frac{1}{i}\vec{\alpha}\cdot\vec{\partial} + \beta m + V_{ext}(\vec{x}) \tag{2.5}$$

$\vec{\alpha}, \beta$ are the well-known Dirac matrices and m is the electron mass.

The quantum state of a many-electron system, $\Psi$, is represented as a functional of the electron-field variable

$$\Psi = \Psi[\varphi, t] \tag{2.6}$$

which depends on a parameter, the time t. (To make this picture complete we would have to express the Hamiltonian H in terms of fields and their canonically adjoint momenta; we do not spell out this formalism in all detail but rather refer to [17] and the literature cited there.)

We should like to reemphasize that equation (2.1) together with the Hamiltonian (2.2) which has the same functional dependence of the electron-field $\varphi(\vec{x})$ for both the non-relativistic and the relativistic case constitute a universal description of many-electron systems. Special relativity only introduces new elements at the level of the single particle dispersion: relativistic kinematics and the fact that A is no longer bounded from below which leads to the interpretation of negative energy states as anti-particles - positrons.

To be definite we shall stick to the non-relativistic case in the following derivations and come back to the relativistic case only at the end of this chapter.

We introduce an infinite dimensional, complete set of single-particle wave functions

$$\{\psi_\alpha(\vec{x})\} \quad : \quad \underline{\text{complete}} \text{ orthonormal set of single-particle wave-functions.} \tag{2.7}$$

and define creation and annihilation operators for electrons

$$a_\alpha^+ = \int d^3x \, \varphi^+(\vec{x})\psi_\alpha(\vec{x})$$
$$a_\alpha := \int d^3x \, \psi_\alpha^*(\vec{x})\varphi(\vec{x}) \tag{2.8}$$

which obey the usual anti-commutation relations

$$[a_\alpha, a_\beta^+]_+ = \delta_{\alpha\beta} \quad , \quad [a_\alpha, a_\beta]_+ = 0 \quad etc \tag{2.9}$$

Many-electron stationary Fock states are then explicitly represented by the functionals

$$\Psi_{\{n_\alpha\}}^{(0)}[\varphi] = \prod_\alpha (a_\alpha^+)^{n_\alpha} \Psi_o^{(0)}$$
$$= \prod_\alpha \left(\int\int d^3x \, \varphi^*(\vec{x})\psi_\alpha(\vec{x})\right)^{n_\alpha} e^{-\int d^3x \, \varphi^*\varphi(\vec{x})} , \tag{2.10}$$

$n_\alpha = 0, 1$ means that the orbital $\psi_\alpha(\vec{x})$ carrying the set of quantum numbers $\alpha$ is unoccupied/occupied; $\Psi_o^{(o)}$ is, of course, the vacuum functional, the set of binaries $\{n_\alpha\}$ denotes a many-electron configuration.

The central problem is now to develop criteria for the optimal choice of $\{\psi_\alpha(\vec{x})\}$ given a many-electron configuration $\{n_\alpha\}$. We take up the traditional approach of using variational principles for attacking this question.

As an illustration consider the expectation value of H taken with the Fock-state corresponding to the configuration $\{n_\alpha\}$

$$\langle\{n_\alpha\}|H|\{n_\alpha\}\rangle = \int D\varphi \, \Psi_{\{n_\alpha\}}^{(o)}[\varphi] \, H \, \Psi_{\{n_\alpha\}}^{(o)}[\varphi] \tag{2.11}$$

$$=: F[\psi_\alpha(\vec{x})] ;$$

we do not spell out the details of the computation of the functional integral since we certainly do not have to convince the reader that F is the well-known Hartree-Fock (HF) functional from which the HF-equation is immediately derived (the variation has to preserve orthonormality, $\varepsilon_\alpha$ is the corresponding Lagrange parameter)

$$\delta F[\psi_\alpha] = 0 \tag{2.12}$$

or

$$(A + \phi_{HF})\psi_\alpha(\vec{x}) = \varepsilon_\alpha \psi_\alpha(\vec{x})$$
$$\phi_{HF}(\vec{x}) = \int d^3x' \, V(\vec{x},\vec{x}')\left\{\sum_\beta n_\beta |\psi_\beta(\vec{x}')|^2 - \psi_\beta^*(\vec{x}')\psi_\beta(\vec{x}')*\right\} . \tag{2.13}$$

Solutions of the stationary Schrödinger equation

$$H \, \Psi_m = E_m \, \Psi_m \tag{2.14}$$

(where $\Psi_m$ is introduced by writing stationary states)

$$\Psi[\varphi,t] = e^{-iE_m t} \Psi_m[\varphi]$$

are then obtained perturbatively [20] from an HF-Goldstone scheme resulting from

rewriting

$$H = \int d^3x \, \varphi^*(\vec{x})\{A + \phi_{HF}\}\varphi(\vec{x})$$
$$+\frac{1}{2}\int d^3x \int d^3x' \, \varphi^*\varphi^*(\vec{x}) V(\vec{x},\vec{x}')\varphi\varphi(\vec{x}') - \int d^3x \, \varphi^*(\vec{x})\phi_{HF}\varphi(\vec{x})\}$$

$$=: H_0 + H_{int}$$
$$(2.15)$$

and perturbing in $H_{int}$.

The point of our paper is now that one can go beyond this construction and obtain a new class of mean-fields. We thus extend the notion of a mean-field and, hence, corroborate the versatility of this concept.

As a first step we enlarge the number of degrees of freedom by introducing the following Hamiltonian

$$\hat{H} = \int d^3x \, \varphi^*(\vec{x})(A + a(\vec{x}))\varphi(\vec{x})$$
$$-\frac{1}{2}\int d^3x \int d^3x' \, a(\vec{x})(V^{-1})(\vec{x},\vec{x}')a(\vec{x}')$$
$$(2.16)$$

where

$$(V^{-1})(\vec{x},\vec{x}') = -\frac{1}{e^2}\,\Delta\,\delta(\vec{x}-\vec{x}')$$
$$(2.17)$$

is the inverse of the Coulomb potential (2.3); a(x) stands for the new degree of freedom and corresponds to the Coulomb field building up the electron-electron interaction. It is clear that H is equivalent to the Hamiltonian (2.2) in any many-electron sector containing only virtual a-quanta: the electron-electron interaction is induced by the exchange of an a-quantum the propagator of which is given by the inverse of $V^{-1}$, i.e. by the Coulomb potential V(x,x').

The real advantage of this formulation appears if we bear in mind that now a richer variational ansatz can be formulated which accounts for the newly acquired degree of freedom. For instance, we could postulate that the a-quanta build up a coherent state

$$\Psi_\phi[a] = e^{-\int d^3x\, \phi(\vec{x})a(\vec{x})}\; e^{-\int d^3x\, a^2(\vec{x})}$$
$$(2.18)$$

and consider the expectation value

$$F[\psi_\alpha;\phi] := \langle\{n_\alpha\},\phi|\hat{H}|\phi,\{n_\alpha\}\rangle$$
$$= \int D a\int D\phi\; \overline{\Psi}_\phi[a]\,\overline{\Psi}^{(0)}_{\{n_\alpha\}}[\varphi]\;\hat{H}\;\Psi^{(0)}_{\{n_\alpha\}}[\varphi]\,\Psi_\phi[a].$$
$$(2.19)$$

We compute

$$F[\psi_\alpha;\phi] = \int d^3x \sum_\alpha n_\alpha \psi_\alpha^*(A+\phi)\psi_\alpha(\vec{x}) - \frac{1}{2}\int\int \phi V^{-1}\phi$$
$$(2.20)$$

and vary as in (2.12) to obtain

$$(A+\phi_H)\psi_\alpha = \varepsilon_\alpha\psi_\alpha$$
$$(2.21)$$

$$\sum_\alpha n_\alpha|\psi_\alpha|^2 - (V^{-1}\phi_H) = 0$$
$$(2.22)$$

The potential $\phi_H$ resulting from (2.22) is immediately recognised as the Hartree potential, (2.21) is the Hartree equation. The corresponding functionals (2.10) comply with the antisymmetry of states required by the Pauli principle and lead to Slater determinants of Hartree orbitals.

The decisive step forward is now to generalise H by introducing a bilocal electromagnetic field potential $\tilde{a}(\vec{x}\vec{x}')$ in order to allow for exchange interactions. The new Hamiltonian reads

$$\hat{H} = \int d^3x\int d^3x'\, \varphi^*(\vec{x})\{A\,\delta(\vec{x}-\vec{x}') + \tilde{a}(\vec{x},\vec{x}')\}\varphi(\vec{x}')$$
$$-\frac{1}{2}\int d^6y\int d^6y'\,\tilde{a}(y)\,\tilde{V}^{-1}(y,y')\,\tilde{a}(y')$$
$$(2.23)$$

where we abbreviated

$$y := (x, x'), \quad y' := (x'', x''')$$

and defined the extended Coulomb potential

$$\widetilde{V}(y,y') = g\,\delta(\bar{x}-\bar{x}')\,\delta(\bar{x}''-\bar{x}''')\,V(\bar{x},\bar{x}'')$$
$$- (1-g)\,\delta(\bar{x}-\bar{x}'')\,\delta(\bar{x}''-\bar{x}')\,V(\bar{x},\bar{x}'). \tag{2.24}$$

The equivalence of $\widehat{H}$ with the Hamiltonian (2.2) in all many-electron sectors is guaranteed by the identity

$$\int d^4x \int d^4x'\,\varphi^*\varphi(\bar{x})\,V(\bar{x},\bar{x}')\,\varphi\,\varphi(\bar{x}') =$$
$$\int d^6y \int d^6y'\,\varphi^*(\bar{x})\,\varphi(\bar{x}')\,\widetilde{V}(y,y')\,\varphi(\bar{x}')\,\varphi(\bar{x}''), \tag{2.25}$$

we see that g drops out identically (the relative sign beetween the g- and (1-g)-term is due to the Pauli principle) and the electron-electron interaction is again given by the Coulomb potential $V(\bar{x},\bar{x}')$. It is easy to see that, in general, g is allowed to be space-dependent.

The variational ansatz for the determination of a mean-field is analogous to (2.19): we construct a coherent state

$$\Psi_{\tilde\phi}[\tilde\alpha] = e^{-\int d^6y\{\tilde\phi(y)\tilde\alpha(y) + \tilde\alpha^*(y)\}} \tag{2.26}$$

and define the functional

$$\widehat{F}[\psi_\alpha;\tilde\phi] := \langle\{n_\alpha\};\tilde\phi\,|\,\widehat{H}\,|\,\tilde\phi;\{n_\alpha\}\rangle$$
$$= \int \mathcal{D}\tilde\alpha \int \mathcal{D}\varphi\,\overline{\Psi}^{(0)}_{\{n_\alpha\}}[\tilde\alpha]\,\overline{\Psi}_{\tilde\phi}[\tilde\alpha]\,\widehat{H}\,\Psi_{\tilde\phi}[\tilde\alpha]\,\Psi^{(0)}_{\{n_\alpha\}}[\tilde\alpha]. \tag{2.27}$$

Performing a variation with a normalisation constraint and integrating the $\delta$-functions in (2.24) we finally obtain the g-Hartree equations

$$(A + \phi_{g-H})\,\psi_\beta = \varepsilon_\beta\,\psi_\beta \tag{2.28}$$

$$\phi_{g-H}(\bar{x}) = \int d^3x'\,V(\bar{x},\bar{x}')\sum_\alpha\{g|\psi_\alpha(\bar{x}')|^2 - (1-g)\,\psi^*_\alpha(\bar{x}')\psi_\beta(\bar{x}')\,*\}. \tag{2.29}$$

The essential idea we employed in order to widen the scope set by the HF-equations was to introduce new bilocal degrees of freedom $a(\bar{x},\bar{x}')$ and to set up a new Hamiltonian $\widehat{H}$ which yields, because of (2.25), a description of electromagnetically interacting systems of electrons entirely equivalent to the one originally given by the Hamiltonian (2.2) containing only electronic degrees of freedom. Quantum states of the system now depend on electromagnetic variables and the frame for physically relevant ansätze is considerably enlarged: putting virtual longitudinal photons in a coherent state leads to the g-Hartree equations.

In the relativistic case the g-Hartree potential resulting from the occupied states is given by (2.29) where the $\psi_\alpha(\bar{x})$ are now Dirac spinors; the deformation of the vacuum by the external and the self-consistent potential, however, leads to an additional contribution [21] leading to small energy shifts.

As we saw in (2.25) the parameter g drops out of the electron-electron interaction functional. Observables, hence, do not depend on it in any exact representation. Approximation schemes, however, do depend on g and the question of an efficient choice arises.

Take for instance the total energy of the many-electron system under consideration

$$E_{tot} = E_{g-H} + E_{corr} \tag{2.30}$$

the splitting of the total energy into a single- particle contribution - the g-Hartree energy

$$E_{g-H} = \sum_\alpha n_\alpha \varepsilon_\alpha + E^{field}_{g-H} = E_{g-H}(g) \tag{2.31}$$

where $E^{field}_{g-H}$ stands for the energy content of the g-Hartree field

$$E^{field}_{g-H} = \int d^3x \int d^3x'\,V(\bar{x},\bar{x}')\sum_\alpha n_\alpha h_\beta\{g|\psi_\alpha(\bar{x}')|^2|\psi_\beta(\bar{x}')|^2$$
$$- (1-g)\,\psi^*_\alpha(\bar{x}')\psi_\alpha(\bar{x})\psi^*_\beta(\bar{x})\psi_\beta(\bar{x}')\} \tag{2.32}$$

and the correlation energy

$$E_{corr} = E_{corr}(g) \tag{2.33}$$

is defined by a Møller-Plesset splitting of the total Hamiltonian (2.2) which is obtained from (2.15) by inserting the g-Hartree potential

There is a choice, $g_0$, for g such that [15]

$$E_{corr}(g)\Big|_{g=g_0} = 0. \qquad (2.34)$$

It seems natural to abstract from these findings a hypothesis for the g-optimisation: the central assumption which was investigated successfully for various atomic observables is the following: an optimal choice, $g_0$, for g results if $g_0$ is chosen such that relevant energy scales - total energies, transition energies etc. - are given by the g-Hartree contribution and, hence, do not contain correlations; correlations in other observables - oscillator strengths, spin-orbit splittings, hyperfine structure etc. - are then small and are thus given by low order terms in the Møller-Plesset perturbation $H_{int}'$.

There is a variety of possibilities to set this hypothesis into practical operation. We discussed the simplest and most straightforward ansätze: assume g is a space-independent constant and determine $g_0$

a) semiphenomenologically from

$$\Delta E_{exp} = \Delta E_{g-H}\Big|_{g=g_0} \qquad (2.35)$$

or

b) ab initio by demanding that the correlation energy computed up to k-th order in $H_{int}$ vanish

$$\Delta E_{corr}^{(k)}\Big|_{g=g_0} = 0 \qquad (2.36)$$

it has been shown [22] that k = 2 yields very satisfactory results for ionisation energies whereas total energies seem to require $k \geq 3$.

If self-consistent potentials become important at large distances (from the centers defined by $V_{ext}(\hat{x})$) the assumption of a constant g might lead to difficulties as can be seen from the following consideration. The equations (2.12), (2.21) and (2.28) are considered to yield orthonormal, complete sets of single-particle orbitals $\{\nu_\alpha\}$: real orbitals with quantum numbers $\alpha$ such that $\nu_\alpha = 1$, virtual orbitals with $\nu_\alpha = 0$. Virtual orbitals of Z-electron systems in particular, "see" an

effective charge

$$Q_{eff} = gZe \qquad (2.37)$$

which, since [23]

$$1/2 \leq g \leq 1 , \qquad (2.38)$$

will, in general, simulate too small shielding effects.

This complication is easily avoided by introducing a space-dependent g and requiring that $g_0$ determined from (2.34 - 36) fulfils the conditions

$$\int d^3x \, g_0(\hat{x}) \sum_h |\nu_h(\hat{x})|^2 = Ze \quad etc. \qquad (2.39)$$

In the following chapter we shall discuss and test a new g-Hartree scenario aiming at molecular structures in which correlations play a prominent role. The underlying idea is an extension of the method of g-optimisation to the configuration interaction method.

We use g-Hartree orbitals as a single-particle basis for CI calculations and treat the g value as an additional variational parameter, i.e. look for a minimum of the total energy of a specific CI calculation as a function of g.

This method is tested numerically for a specific model for which the full CI solution, i.e. the solution of the Schrödinger equation for the projection of the exact non-relativistic Hamiltonian to the finite space generated from the given LCAO basis set, is known. We choose the so-called double-zeta water, a quantum mechanical model for the water molecule in an LCAO expansion employing fourteen cartesian gaussian functions [24,25], which can be considered a standard model for the test of any method for the calculation of correlation effects [26-28].

Thus we restrict ourselves to only one of the aspects introduced into atomic and molecular structure theory by single-particle basis sets, namely the one connected with the construction of multi-particle configuration state functions. The impact of the g-Hartree theory on the determination of the LCAO basis set will be investigated in a separate publication.

## 3. TECHNICAL DETAILS

We present results for the water molecule at three bond distances (R = R_e, R = 1.5 R_e and R = 2R_e, R_e denoting the equilibrium bond distance). The calculations are carried out in the double zeta basis set which has also been used for the full CI reported in [24] and [25]. Our values of the Hartree-Fock self-consistent field energy are -76.009838, -75.803529 and -75.595180 atomic units, respectively, and agree with those given in [25] to all significant figures.

We employed the CI package of Buenker and Peyerimhoff [29-30] to compare CI results using Hartree-Fock orbitals with corresponding values based on g-Hartree orbitals, as well as those from approximate natural orbitals, obtained from diagonalizing the CI density matrix of a singles-doubles (SD-CI) calculation with Hartree-Fock orbitals. We also report SDT-CI results, calculated by generating all double excitations of a reference set comprising the Hartree-Fock configuration and its 19 single excitations. Besides the lowest eigenvalue of the secular equation we give the generalized Davidson correction [31-33] to extrapolate to the full CI result by adding

$$\Delta E = (1 - \sum c_{ref}^2)(E_{ref} - E_{CI})$$

to the eigenvalue, whereby $\sum c_{ref}^2$ denotes the sum of squares of the coefficients of any reference configuration state function in the final wave function, and $E_{ref}$ the eigenvalue of the lowest root of the reference space. Results near to full CI quality are obtained from MRD-CI (multi-reference double excitation) calculations performed by adding all configurations developing coefficients with a square larger than 0.002 in the SDT-CI wave function to the reference set, from which all single and double substitutions are generated.

In figure 1 we give the percentage of correlation energy recovered as function of the number of configuration state functions employed in the corresponding CI calculation. The configurations are ordered in this case by the size of their second order coupling with the lowest root of the reference set employed (the Hartree-Fock

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¹coordinates of the atoms in atomic units: H (±1.515263, -1.058898, 0.).
0 (0., 0., -0.009)

²H (±2.27289, -1.574847, 0.), 0(0., 0., 0.)

³H (±3.03053, -2.09980, 0.), 0(0., 0., 0.)

configuration in figs. 1a,c,e,g and the Hartree-Fock configuration plus all single excitations in figs. 1b,d,f,h). In practice, the selection has been carried out using the selection features of the MRD-CI package [29] by specifying a certain threshold and selecting a configuration if the arithmetic mean of the second order coupling of its configuration state functions to the reference set exceeds that threshold.

## 4. RESULTS OF THE CALCULATIONS

Table 1 presents the results of various CI calculations employing Hartree-Fock and g-Hartree orbitals, tabulated for the g-value that maximise the correlation energy for the given CI type.

Perhaps the most striking difference to Hartree-Fock orbitals is the fact that already the singles CI (S-CI) (comprising only 20 configuration state functions) recovers a considerable percentage of correlation energy in the case of g-Hartree orbitals. In the Hartree-Fock case, the singles do not contribute to the energy by the Brillouin theorem. From table 1 we also infer that in our specific case the singles-doubles-triples (SDT) CI employing g-Hartree orbitals recovers a considerably larger portion of correlation energy than the HF-orbital calculation (up to 7 % more in the case R = 2 R_e, showing the largest correlations). The Davidson correction gives reliable full CI estimates except for the latter case already at the SDT level. Since the maximum of the correlation energy recovered occurs for the S-CI and the SDT-CI at almost the same g-values, a simplified computational procedure might be devised from determining the minimum energy of a S-CI calculation as function of g and then using this g-value for an SDT-CI or an MRD-CI calculation. From table 1 we also see that an MRD-CI calculation using Hartree-Fock orbitals requires 20 % larger CI expansions to recover 99 % correlation energy, ensuring a full CI estimate that agrees with the full CI value within 0.5 %. Of course, g-Hartree orbitals also compete with more elaborate MCSCF- and CASSCF orbitals. A calculation for the equilibrium geometry corresponding to the treatment above gives 95.5 % on the SDT-CI level (99.54 % after full CI correction), starting from a CASSCF calculation with 8 active orbitals, recovering itself 82.5 % of the correlation energy with 492 CSFs. This result again illustrates the effect of unitary invariance in the occupied space, which is approximately retained in the CASSCF procedure. An MRD-CI calculation employing these CASSCF orbitals yields finally 99.6 % (using 7290 CSFs), and a full CI estimate 100.31 % of the total correlation energy [34]. Despite this good result we should bear in mind that it was ob-

tained using orbitals from a rather costly procedure, as compared with the g-Hartree mean field calculation, and results in a CI expansion that is much larger than the corresponding one in the g-Hartree approach.

Since it may be considered too expensive to reoptimise the g-value for all bond distances, we give in table 2 the results obtained from g-Hartree orbitals for a fixed value g = 0.78. The favorable performance of the g-Hartree orbitals for a fixed value g = 0.78. The favorable performance of the g-Hartree orbitals for a fixed value g = 0.78 is still striking.

Table 3 gives the results obtained from an SD-CI calculation. In marked difference to the S-CI and SDl-CI results, we see that the minimum of the SD-CI energy occurs at quite different g-values (0.88, 0.86 and 0.71), which are, however, near to the minimum of the expectation value of a single Slater determinant as a function of g. The correlation energy percentage recovered with this treatment is well below the HF result, showing that the tadpole graphs in the perturbation expansion around the g-Hartree mean field [15] have great importance. Only if these graphs are present, as in a S-CI or a SDT-CI treatment, the g-Hartree orbitals turn out to be superior to Hartree-Fock orbitals. We note that due to the Brillouin theorem, the SDT level gives almost no improvement over the SD-CI result when using Hartree-Fock orbitals. In this case, the next jump occurs for the SDTQ result (99.8 %, 99.5 % and 98.6 %) [25].

Since CI calculations often employ configuration selection techniques, it would be interesting to study the properties of g-Hartree orbitals compared with Hartree-Fock and natural orbitals in CI expansions shorter than a full class CI. Corresponding results are summarized in figures 1a - 1h. The broken lines with squares denote CI calculations employing Hartree-Fock orbitals, full lines with circles denote natural orbitals from a HF-SDCI, and the dashed-dotted lines with triangles the g-Hartree calculation. Only for the equilibrium geometry (a - d), we give the g=0.78 and g=0.88 result. Figures 1a,c,e,g refer to selection from an SD-CI, Figs. 1b,d,f,h to selection from SDT-CI. Figures 1c and 1d give details of figures 1a and 1b respectively, and 1e-1h refer to the larger bond distances, for which g = 0.78 results are shown. We see that for selection from SD-CI the g-Hartree orbitals hardly show any advantage, whereas for selection from SDT-CI the g-Hartree orbitals soon turn out to be superior, the improvement being most significant in the case with largest correlations, R = 2 R$_e$.

For natural orbitals we essentially reproduce the results of [8], showing a definite advantage for very short expansions, which diminishes very soon going to SD-CI or beyond.

As an interesting feature we may note the kink exhibited by the HF curve in the case of selection from an SD-CI. Single excitations will not be selected by the MRD-CI procedure (unless explicitly requested) due to their vanishing coupling with the

reference configuration, but on the other hand, higher order couplings involving single excitations contribute considerably to the correlation energy at larger bond distances. As a consequence, any extrapolation from the selected Hartree-Fock configuration spaces to the SD-CI limit is dangerous in this case and gives values turning out much too low. This is reminiscent of a situation encountered already in a different context [35], an undue selection also preventing reliable extrapolation. In the present case the difficulty may be traced down entirely to the properties of single excitations with respect to a Hartree-Fock determinant.

5. CONCLUSIONS

Our first aim was to show that the scope of mean-field equations for the determination of single-electron orbitals building up the source of a self-consistent electromagnetic field can be considerably enlarged by introducing electromagnetic degrees of freedom into the traditional variational principles. The introduction of a local dynamical Coulomb field led to the Hartree, a bilocal generalisation allowing for exchange forces to the g-Hartree equations. The latter involve a modification of exchange and direct interactions by factors g and 1-g, respectively, where g is, in general, space-dependent.

This mean-field theory has two applications in practical electronic structure calculations: The determination of the parameter of the LCAO basis set by g-Hartree methods (instead of Hartree-Fock calculations) and the optimisation of the single-particle basis set from which configuration state functions for configuration interaction are generated ("molecular orbitals"). We investigated the latter aspect and showed, taking g to be constant, that g-Hartree orbitals offer definite advantages in the specific case of the water molecule in a double-zeta basis set, if only a CI method is used that appropriately includes single-particle excitations, as e.g. SDT-CI or MRD-CI. The improvements introduced by g-Hartree orbitals is especially notable in the case of large correlations.

It remains to be investigated if the findings for double zeta water carry over to more realistic systems, and if the optimal g-value can be calculated economically from low order approximations, as it was the case in the current study. The implementation of a g-Hartree mean field with space dependent g appears to be important in this context in order to effect a more detailed description of shielding already in the mean field itself.

As a general conclusion, we should emphasise that the g-Hartree theory constitutes a rather general framework for the determination of self-consistent mean-fields, it is by no means true that the Hartree-Fock scheme is in any sense the unique formal realisation of the physical concept of an average field produced by N-1 electrons in an N-electron system. On the contrary, this concept leads as well to the less restrictive g-Hartree formulation of mean-field equations.

It is important to use the apparent freedom contained in the latter in a judicious manner which should be solely dictated by the general physical characteristics of the problem considered. For example, approximation schemes within the g-Hartree theory which proved useful in problems with small correlations should not be blindly applied to problems with large correlations.

At this point one might question the predictive power of mean-field theory. Indeed, the picture which seems to emerge is that for any atomic or molecular observable a mean-field can be found such that it allows for its exact calculation (in the sense that quantum fluctuations vanish for this particular observable). The predictiveness of the scheme which we anticipate (and which was shown to operate successfully in the cases considered) lies in the hypothesis that by determining the mean-field for one observable, preferably the energy, such that higher perturbative corrections vanish we also suppress correlations in other observables, i.e. a perturbative calculation (perturbing around this mean-field) of other observables is rapidly converging and requires only low orders. The practical importance of such a scheme is obvious.

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Fig. 1

Percentage of correlation energy for double-zeta water recovered from various CI spaces as a function of the dimension of that space. The molecular orbital basis sets employed are denoted as follows:

————o———          natural orbitals from singles-doubles CI

----□---              Hartree-Fock SCF orbitals

—·—△—·.           $g$-Hartree orbitals ($g$ = 0.78)

—··—▽—··           $g$-Hartree orbitals ($g$ = 0.88)

1a) equilibrium geometry; selection from singles-doubles (SD) CI

1b) equilibrium geometry; selection from singles-doubles-triples (SDT) CI

1c) detail of 1a)

1d) detail of 1b)

1e) R = 1.5 $R_e$; selection from SD-CI

1f) R = 1.5 $R_e$; selection from SDT-CI

1g) R = 2 $R_e$; selection from SD-CI

1h) R = 2$R_e$; selection from SDT-CI

## Table 1

Percentage of correlation energy recovered in various CI calculations on double zeta water

| | no of CSF's | % corr. energy HF orbitals | % corr. energy gH orbitals | g value | % corr. energy HF orbitals DC[1] | % corr. energy gH orbitals DC[1] |
|---|---|---|---|---|---|---|
| **R=R_e [2]** | | | | | | |
| S-CI[3] | 20 | 0.00 | 46.39 | 0.763 | | |
| SDT-CI[4] | 3203 | 95.47 | 98.62 | 0.770 | 99.54 | 99.80 |
| MRD-CI[5] | 5267 | 98.18 | [6] | | 100.98 | |
| **R=1.5R_e [7]** | | | | | | |
| S-CI | 20 | 0.00 | 36.82 | 0.780 | | |
| SDT-CI | 3203 | 91.15 | 96.00 | 0.780 | 100.91 | 100.46 |
| MRD-CI | 4823 | | 98.87 | 0.760 | | 100.27 |
| | 7024 | 98.93 | | | 100.45 | |
| **R=2R_e [8]** | | | | | | |
| S-CI | 20 | 0.00 | 29.03 | 0.780 | | |
| SDT-CI | 3203 | 83.96 | 91.39 | 0.780 | 105.49 | 105.96 |
| MRD-CI | 4981 | | 99.30 | 0.757 | | 100.40 |
| | 6138 | 98.30 | | | 100.48 | |

[1] Energy including generalized Davidson correction $\Delta E = (1 - \sum c_{ref}^2)(E_{ref} - E_{MRD-CI})$. $E_{ref}$ denoting the energy value in the reference space and $\sum c_{ref}^2$ the sum of squares of the coefficients of all reference configurations in the final wave function.

[2] equilibrium geometry. The HF-SCF energy is -76.009838 a.u., the full CI energy is -76.157866 a.u.

[3] CI calculation comprising all single excitations with respect to the ground state configuration.

[4] CI calculation comprising all single, double and triple excitations with respect to the ground state configuration.

[5] Multi-reference double excitation configuration, comprising all double excitations with respect to any configuration that has a configuration state function with $c^2 > 0.002$, $c$ denoting the coefficient of the CSF in the SDT-CI wave function.

[6] all configurations with $c^2 > 0.002$ are single excitations to the ground state configuration.

[7] The HF-SCF energy is -75.803529 a.u., the full CI energy is -76.014521 a.u.

[8] The HF-SCF energy is -75.595180 a.u., the full CI energy is -75.905247 a.u.

## Table 2

g-Hartree calculations on double zeta water using a fixed value of g = 0.78.
(percentage of total correlation energy)

| | R=R_e | R=1.5R_e | R=2R_e |
|---|---|---|---|
| S-CI | 43.9 | 36.8 | 29.0 |
| SD-CI | 78.3 | 68.6 | 62.6 |
| SDT-CI | 98.5 | 96.0 | 91.4 |
| HF-SD-CI | 94.7 | 89.4 | 80.5 |
| HF-SDT-CI | 95.5 | 91.1 | 84.0 |

## Table 3

SD-CI results at the minimum of g variation

| | R=R_e | R=1.5R_e | R=2R_e |
|---|---|---|---|
| optimal g | 0.88 | 0.86[1] | 0.71[2] |
| % corr. energy | 93.2 | 83.7 | 74.0 |
| HF-SD | 94.7 | 89.4 | 80.5 |

[1] no convergence obtained for higher values of g.

[2] below g = 0.78, the ground state mean field configuration does not have the largest weight in the first root of a SD-CI

**Fig. 1b**

% CORRELATION ENERGY

20  40  60  80  100

NUMBER OF CONFIGURATIONS

20  100  1000

**Fig. 1a**

% CORRELATION ENERGY

0  20  40  60  80  100

NUMBER OF CONFIGURATIONS

1  10  100

**Fig. 1d**

% CORRELATION ENERGY

80  90  100

NUMBER OF CONFIGURATIONS

100  500  1000

**Fig. 1c**

% CORRELATION ENERGY

60  70  80  90  100

NUMBER OF CONFIGURATIONS

100  200  300  400

% CORRELATION ENERGY

NUMBER OF CONFIGURATIONS

Fig.1g

100

50

0

100

10

1

% CORRELATION ENERGY

NUMBER OF CONFIGURATIONS

Fig.1h

100

50

0

1000

100

20

% CORRELATION ENERGY

NUMBER OF CONFIGURATIONS

Fig.1e

100

50

0

$10^2$

$10^1$

$10^0$

% CORRELATION ENERGY

NUMBER OF CONFIGURATIONS

Fig.1f

100

80

60

40

20

0

1000

100

20